

A $\sim 32\text{-}70$ K formation temperature range for the ice grains agglomerated by comet 67P/Churyumov-Gerasimenko

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ABSTRACT

Grand Canonical Monte Carlo simulations are used to reproduce the N_2/CO ratio ranging between 1.7×10^{-3} and 1.6×10^{-2} observed *in situ* in the Jupiter family comet 67P/Churyumov-Gerasimenko by the ROSINA mass spectrometer aboard the Rosetta spacecraft, assuming that this body has been agglomerated from clathrates in the protosolar nebula. Simulations are done using an elaborated interatomic potentials for investigating the temperature dependence of the trapping within a multiple guest clathrate formed from a gas mixture of CO and N_2 in proportions corresponding to those expected for the protosolar nebula. By assuming that 67P/Churyumov-Gerasimenko agglomerated from clathrates, our calculations suggest the cometary grains must have been formed at temperatures ranging between ~ 31.8 and 69.9 K in the protosolar nebula to match the N_2/CO ratio measured by the ROSINA mass spectrometer. The presence of clathrates in Jupiter family comets could then explain the potential N_2 depletion (factor up to ~ 87 compared to the protosolar value) measured in 67P/Churyumov-Gerasimenko.

Subject headings: astrobiology – comets: general – comets: individual
(67P/Churyumov-Gerasimenko) – solid state: volatile – methods: numerical

1. Introduction

The thermodynamic conditions prevailing in many bodies of the solar system suggest that clathrates could exist in the Martian permafrost (Thomas et al. 2009; Swindle et al. 2009; Mousis et al. 2013), on Titan (Choukroun & Sotin 2012; Mousis et al. 2014), as well as in the interiors of other icy satellites (Kieffer et al. 2006; Hand et al. 2006). It has also been suggested that the activity observed in some cometary nuclei results from the dissociation of these crystalline structures (Marconi & Mendis 1983; Smoluchowski 1988; Marboeuf et al. 2010, 2011, 2012; Mousis et al. 2012). Several indirect evidences suggest that clathrates probably participated in the formation of planetesimals and the building blocks of giant planets in the outer solar system (Lunine & Stevenson 1985; Mousis et al. 2010, 2014).

In the absence of experimental data existing at low-temperature (20–200 K) and low-pressure conditions (10^{-13} – 10^{-3} bar), which are typical of those encountered in planetary environments (Lunine & Stevenson 1985; Sloan & Koh 2008), clathrates are characterized via theoretical modeling. The approach usually employed in planetary science is based on the statistical mechanics model initially proposed by van der Waals & Platteeuw (1959), which makes use of simplified intermolecular potentials calibrated on equilibrium measurements performed at relatively high temperatures. In consequence, the use of these potentials at thermodynamic conditions relevant to those of the protosolar nebula (hereafter PSN) for predicting the composition of clathrates deserves to be confronted with more sophisticated approaches.

In this present work, we aim at reproducing the N_2/CO ratio ranging between 1.7×10^{-3} and 1.6×10^{-2} observed *in situ* in the Jupiter family comet 67P/Churyumov-Gerasimenko (hereafter 67P) by the ROSINA mass spectrometer aboard the Rosetta spacecraft (Balsiger et al. 2007), which is found to be depleted by a factor up to ~ 87 compared to the value of 0.148 hypothesized for the protosolar nebula (see below). By

assuming that 67P has been agglomerated from clathrates, it is possible to derive the temperature range of formation of these crystalline structures in the PSN by mean of Grand Canonical Monte Carlo (GCMC) simulations based on elaborated interatomic potentials. These allowed us to investigate the temperature dependence of the trapping within a multiple guest (hereafter MG) clathrate formed from a gaseous mixture of CO and N₂ in proportions corresponding to those expected for the protosolar nebula.

2. Computational details and simulation procedure

We assume multiple guest (MG) clathrate formation from a gaseous mixture composed of N₂ and CO in proportions specified from a plausible protosolar gas phase composition. For this, we have assumed that both all C and N are in form of CO and N₂ in the initial disk’s gas phase. This assumption is in agreement with thermochemical models of the protosolar nebula (Lewis & Prinn 1980; Prinn & Fegley 1989; Mousis et al. 2002). The use of C and N protosolar elemental abundances from the compilation of Lodders et al. (2009) allowed us to derive a gaseous mixture with mole fractions of 0.871 for CO and 0.129 for N₂, giving a N₂/CO ratio of 0.148 in the PSN.

The MG clathrate composition has been computed along its equilibrium pressure curve $P_{\text{eq},MG}$ given by (Thomas et al. 2007; Mousis & Schmitt 2008):

$$P_{\text{eq},MG} = \left[\sum_i \frac{y_i}{P_{\text{eq},i}} \right]^{-1}, \quad (1)$$

where y_i is the mole fraction of species i in the gas phase (here CO or N₂) and $P_{\text{eq},i}$ the equilibrium pressure of single guest clathrate formed from component i only.

The equilibrium pressures $P_{\text{eq},i}$ (in bar) are determined by using an equation based on an Arrhenius law (Miller 1961):

$$\ln P_{\text{eq},i} = \frac{A_i}{T} + B_i, \quad (2)$$

where A_i and B_i are constant parameters depending on the nature of the species trapped in the clathrate and T is the temperature (K). A_i and B_i have been determined by fitting the available theoretical and laboratory data (Mousis et al. 2008) and their values are given in Table 1. The calculated values of $P_{\text{eq},i}$ and partial pressures of CO (P_{CO}) and N₂ (P_{N_2}) are represented as a function of the inverse temperature in Fig. 1. Here, the equilibrium pressure of MG clathrate is in the $\sim 5.2 \times 10^{-10}$ – 2.9×10^{-3} bar range when T is varied between ~ 52 and 100 K, respectively.

We have calculated the composition of N₂–CO clathrates via Monte-carlo (MC) simulations in the Grand Canonical ensemble (GCMC) (Frenkel & Smit 2002) for temperatures ranging from 52 to 100 K (the choice of this temperature range is explained in Sec. 3, but it is worth noting that, below 50 K, the equilibration time is in fact too long for the GCMC simulation), with an increment of 4 K between each computation. All our calculations have been performed in the case of Structure I (SI) clathrates (see structural details in Sloan & Koh (2008)). This choice has been motivated by the fact that CO is the dominating species in the gaseous mixture and is known to form Structure I single guest clathrate (Mohammadi 2005).

In our system, the considered crystal size consists in 125 cubic unit cells ($5 \times 5 \times 5$), corresponding to 5,750 water molecules. The dimension of one parameter of the cubic simulation box is set equal to 60.15 Å during all our simulations. Periodic boundary conditions are applied to mimic infinite crystal. The water molecules are modeled using the well-known TIP4P/2005 model (Abascal & Vega 2005), allowing them to translate and rotate during the simulation. Models for N₂ and CO molecules are taken from Potoff & Siepmann (2001) and Piper et al. (1984), respectively. One hundred million MC steps were

performed including insertion, deletion, translation and rotation of the molecules. Only the last 50 million steps were used to compute the data. The first 50 million steps have been discarded from the analysis and were only used to equilibrate the system.

From the knowledge of the partial pressure of each species (see Fig. 1), GCMC simulations have been performed to compute the composition of the MG clathrate. However, the number of MC steps needed to equilibrate the system strongly increases when temperature decreases. Simulation tests showed that below a temperature of 52 K, this number becomes even larger than the 50 million steps we simulated. At these low temperatures, statistically relevant results on the mole fractions of encaged molecules in our MC calculations thus become too time consuming. In consequence, below 52 K, these quantities have been evaluated via a thermodynamic extrapolation, described below, and fitted to the results computed at higher temperatures.

After the equilibration period, chemical equilibrium takes place between gas and clathrate. It is then possible to write an equilibrium constant K_i for each species i in the form:

$$K_i = \frac{a_i}{P_i/P^0}, \quad (3)$$

where a_i is the activity of species i in clathrate defined from the mole fraction of species i in clathrate (x_i) and its activity coefficient (γ_i) as $a_i = \gamma_i x_i$. The evolution of K_i with temperature should obey the Van't Hoff relation:

$$\frac{d \ln K_i}{dT} = \frac{\Delta E_i}{RT^2}, \quad (4)$$

where ΔE_i is the entrapping energy of CO or N₂, and R the ideal gas constant.

Under the simulated conditions, the occupancy of the clathrate cages is still maximum.

We thus, obtained an amount of 8 molecules of CO and N₂ per unit cell, implying that the total number of molecules trapped in clathrate is constant, independently of the temperature. By Neglecting the non ideal terms of the activity coefficient at first approximation, this allowed us to get $\gamma_i = 1$ and to rewrite Eq. 4 as follows:

$$\frac{d\ln(N_i/P_i)}{d(1/T)} = -\frac{\Delta E_i}{R}, \quad (5)$$

with N_i the number of encaged molecules of type i . Our simulations allowed retrieving the values of N_{CO} and N_{N_2} at temperatures higher than 52 K and provided us with a direct access to the different values of the quantity $\ln(N_i/P_i)$. Figure 2 represents these quantities plotted for CO and N₂ as a function of $1/T$. They show a linear behavior with a correlation coefficient higher than 0.999 for each species, in agreement with Eq. 5. The computed data have been fitted via the use of linear equations, allowing to find $\ln(N_{\text{CO}}/P_{\text{CO}}) = 1685.145/T - 15.617$ and $\ln(N_{\text{N}_2}/P_{\text{N}_2}) = 1554.469/T - 15.972$. The entrapping energies comes directly from the fit, $\Delta E_{\text{CO}} = -1685.145 \times R$ and $\Delta E_{\text{N}_2} = -1554.469 \times R$. These two linear equations have been used to estimate the $N_{\text{N}_2}/N_{\text{CO}}$ ratio at temperatures lower than 52 K. Note that, for simplification, we will use below the abbreviation N₂/CO for this ratio.

3. Results

Figure 3 shows the evolution of N₂/CO ratio as a function of temperature in the 20–100 K range. This ratio monotonically increases with the growing temperature. The figure exhibits a linear regime in the 50–100 K range whereas at lower temperatures, the curve trend is less steep and the ratio converges smoothly towards zero. The N₂/CO ratio found is equal to $\sim 1.5 \times 10^{-4}$ at 20 K. This value is 50 times smaller than at 50 K. In the temperature range considered here, the calculated N₂/CO ratio is significantly lower than

the ratio of ~ 0.15 in the coexisting gas phase. This indicates that the clathrate formation favors the CO entrapping at the expense of N_2 . This behavior is related to the difference in entrapping energy between CO and N_2 . Indeed, ΔE_{CO} being lower, the entrapping of CO is selectively favored when the temperature decreases.

Figure 4 is a zoom of a portion of Fig. 3 given for easy reading of the correspondence between the N_2/CO ratio measured in 67P by the ROSINA instrument and the formation temperature of the ice grains from which the comet agglomerated. Taking into account the strong variation of the N_2/CO measurement between 0.17 to 1.6% depending on the position of the Rosetta spacecraft above the surface of the comet nucleus (Rubin et al. 2015), we find that the ice grains at the origin of 67P formed at temperatures ranging between ~ 31.8 and 69.9 K in the protosolar nebula, with corresponding equilibrium pressures ranging between 6.0×10^{-19} and 2.1×10^{-6} bar. For the sake of information, the mean N_2/CO ratio of 0.57% corresponding to the averaging of the 138 spectra obtained by Rubin et al. (2015) is represented on Fig. 4. The corresponding formation temperature of the ice grains is of ~ 45 K in the PSN, with an equilibrium pressure of 3.3×10^{-12} bar.

4. Discussion and Conclusions

The composition of a MG clathrate formed from a gaseous mixture of N_2 and CO in proportions corresponding to those expected for the protosolar nebula (87.1 % for CO and 12.9% for N_2) has been investigated in the 20–100 K temperature range. Above 50 K, the clathrate composition has been computed via Grand Canonical Monte-Carlo simulations for pressures ranging from $\sim 5.2 \times 10^{-10}$ to 2.9×10^{-3} bar. Below 50 K, the clathrate composition has been extrapolated via the use of a Van't Hoff relation. The results show that, at thermodynamic conditions relevant to those of the protosolar nebula, CO has a much higher propensity than N_2 to be trapped in clathrates. Assuming that

67P agglomerated from clathrates, our calculations suggest that the cometary grains must have formed at temperatures ranging between ~ 31.8 and 69.9 K in the protosolar nebula to match the N_2/CO ratio measured by the ROSINA mass spectrometer (Rubin et al. 2015).

Whilst narrower, the range of formation temperatures inferred from our model for the grains of 67P is consistent with the one ($\sim 22\text{--}80$ K) found from the reading of Fig. 2 of Mousis et al. (2012) who performed calculations of planetesimals compositions based on the classical statistical mechanics model of van der Waals & Platteeuw (1959). In the absence of experiments at this temperature range, the fact that these two different approaches lead to similar conclusions, namely that clathrates can explain the N_2/CO ratio observed in 67P, suggest that this scenario is plausible. The presence of clathrates in Jupiter family comets could then explain the apparent N_2 depletion (factor up to ~ 87 compared to the protosolar value) measured in 67P.

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Table 1: Parameters of the equilibrium curves of the considered single guest clathrates

Molecule type i	A_i / (K)	B_i
CO	-1685.54	10.9946
N ₂	-1677.62	11.1919

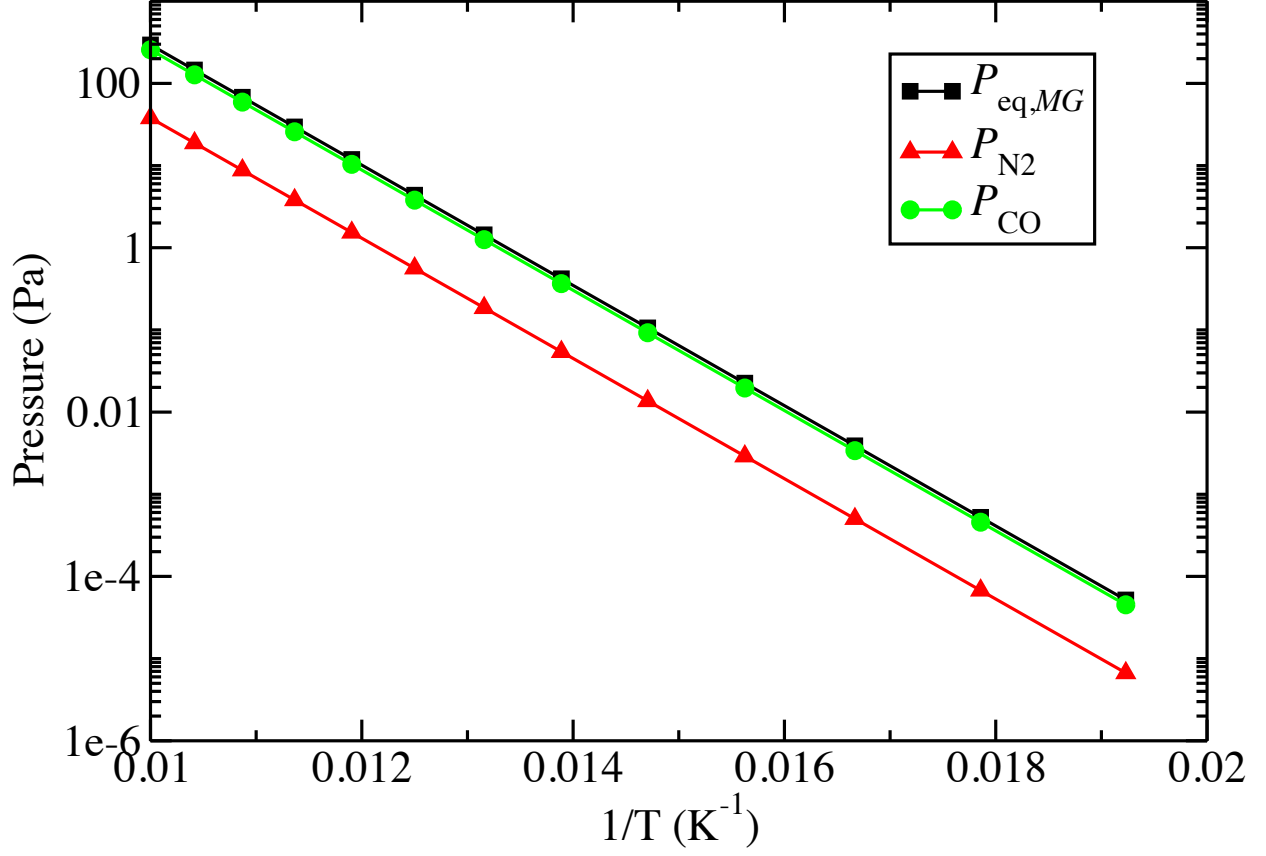


Fig. 1.— Calculated pressure and partial pressures of CO and N₂ in the gas as a function of the inverse temperature based on the Arrhenius law and using parameters in Table 1.

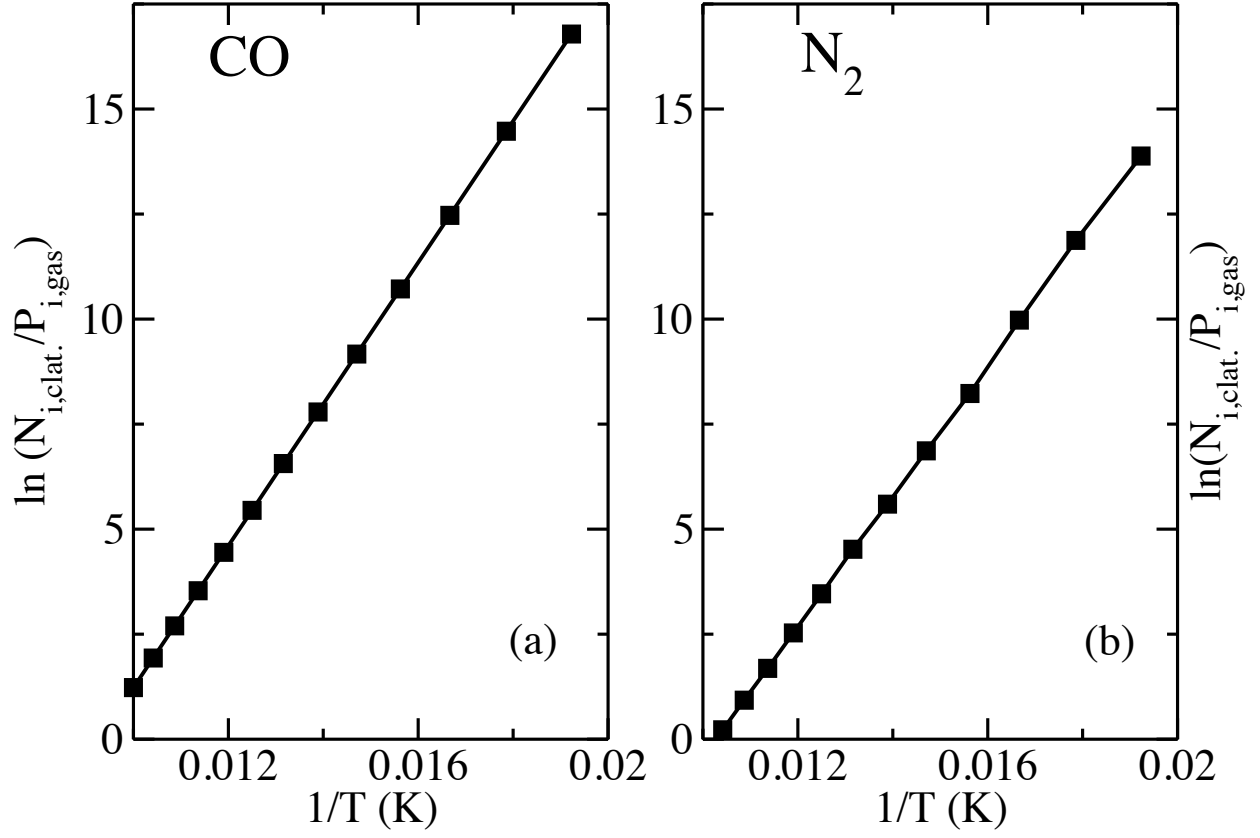


Fig. 2.— Evolution of the number of encaged molecules in the cases of CO (a) and N_2 (b) as a function of the inverse temperature. A linear fit was performed on the data with correlation coefficients higher than 0.999 in both cases (see text). The figure shows the results of the GCMC simulation between 52K and 100K.

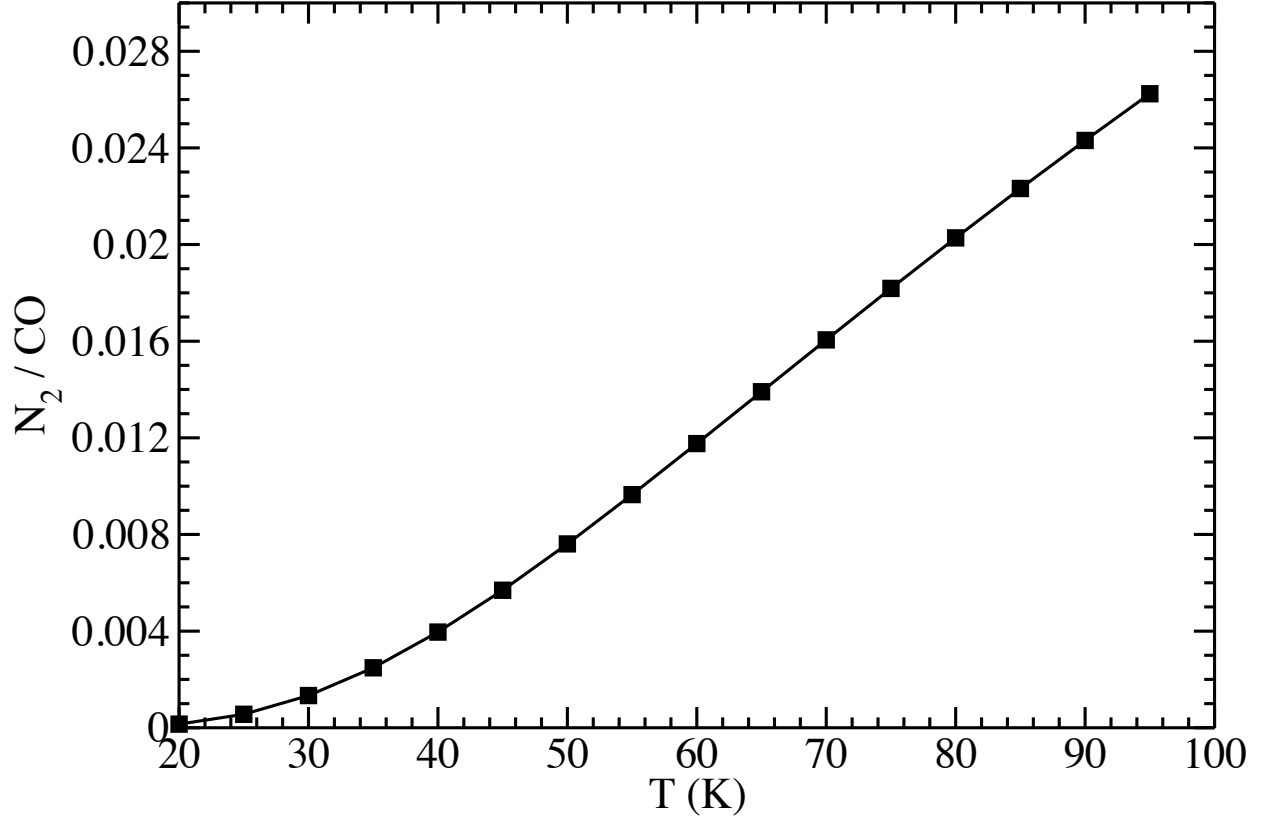


Fig. 3.— N_2/CO ratio in clathrate as a function of formation temperature. The results are derived from the GCMC simulations performed above 52K. Below this temperature, they are based on the entrapping energies derived from the GCMC simulations.

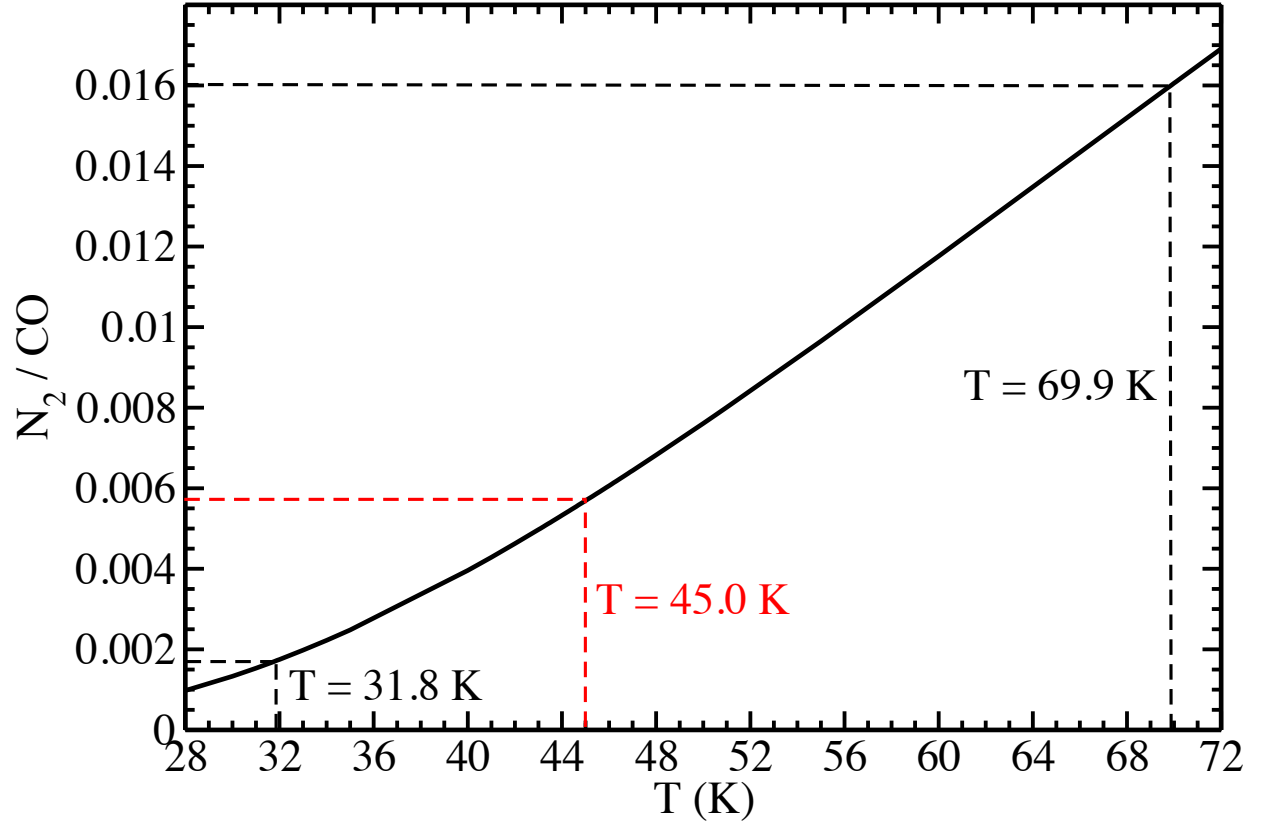


Fig. 4.— Minimum and maximum N_2/CO ratios measured in 67P and corresponding formation temperatures for the ice grains. The results are derived from the GCMC simulations performed above 52K. Below this temperature, they are based on the entrapping energies derived from the GCMC simulations.